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MINERALS FROM MACEDONIA

V. CHARACTERIZATION OF GYPSUM, BARITE AND THEIR SYNTHETIC ANALOGUES BY FTIR AND RAMAN SPECTROSCOPY

Viktor Stefov[1], Gligor Jovanovski[1*], Bojan Šoptrajanov[1], Biljana Minčeva-Šukarova[1], Sandra Dimitrovska[1], Blažo Boev[2]

[1]*Faculty of Sciences, Institute of Chemistry, P.O. Box 162, MK-1001 Skopje, Republic of Macedonia, e-mail: gligor@pmf.ukim.edu.mk*
[2]*Faculty of Mining and Geology, Goce Delčev 89, MK-2000 Štip, Republic of Macedonia, e-mail: b.boev@rgf.ukim.edu.mk*

A b s t r a c t: The Fourier transform infrared (FTIR) and Raman spectra of gypsum ($CaSO_4 \cdot 2H_2O$) and barite ($BaSO_4$) from various localities in Macedonia were studied. Contrary to the group-theoretical predictions, it was found that the band originating from the ν_2 sulfate mode (expected at around 450 cm^{-1}) does not appear in the infrared spectra of either gypsum or barite, apparently due to the high *effective* symmetry of the force field for this mode. The infrared and Raman spectra of natural gypsum and its synthetic analogue are very similar. On the other hand, slight frequency differences (especially pronounced in the region of the ν_3 sulfate modes) were registered in the infrared spectrum (and, to a considerably lesser extent in the Raman spectrum as well) of synthetic $BaSO_4$ when compared to the spectrum of mineral barite. Also studied were the FTIR and Raman spectra of a mineral previously characterized as anhydrite. Although its morphological characteristics (shape, color and transparency) were quite different from those of gypsum it was shown that the studied mineral is in fact gypsum.

Key words: sulfate minerals; gypsum; barite; Macedonia; FTIR and Raman spectroscopy

INTRODUCTION

Sulfate minerals have been studied by various methods, the most frequently used complementary techniques for their characterization being X-ray diffraction (e.g., Bish and Post, 1993), Raman (see, e.g., Coleyshaw and Griffith, 1994) and infrared spectroscopy (e.g., Farmer, 1974). The infrared and Raman spectra of gypsum and barite have been a subject of extensive studies by various authors (Omori and Kerr, 1963; Berenblut *et al.*, 1971; Takahashi *et al.*, 1983; Petruševski and Šoptrajanov, 1984; Peterson, 1986; Petruševski, 1989; Cvetković *et al.*, 1997). The infrared spectra of the partially deuterated analogues of gypsum have also been studied (Seidl *et al.*, 1969).

Continuing our studies of the structural and spectroscopic characteristics of minerals originating from Macedonia (Stefov *et al.*, 1999; Jovanovski *et al.*, 1999a; G. Jovanovski *et al.*, 1999b; G. Jovanovski *et al.*, 1999c) we present the results of the collection, detection and spectroscopic characterization of mineral specimens of gypsum ($CaSO_4 \cdot 2H_2O$) and barite ($BaSO_4$) from various localities in Macedonia (Debar, Alshar and Plešinci for gypsum and Zletovo for barite) using Fourier transform infrared (FTIR) and Raman spectroscopy (some preliminary infrared results for gypsum and barite were reported earlier (Stefov *et al.*, 1999). In addition to that, in the current paper we present the results of the comparison of the IR and Raman spectra of gypsum and barite and of their synthetic analogues as well as the outcome of the investigation of a mineral specimen from Debar identified, on morphological grounds, as anhydrite ($CaSO_4$).

It is well known that gypsum crystallizes in the monoclinic system (space group *C2/c*) (Pedersen and Semmingsen, 1982), whereas barite is orthorhombic (space group *Pnma*) (Bragg and Clar-

*Corresponding author. Tel. +389 2 117 055; fax: +389 2 226 865; e-mail:gligor@pmf.ukim.edu.mk

ingbull, 1965). Although for "free" SO_4^{2-} ions the symmetry should be T_d, the presence of other ions in the respective crystal lattices reduces their symmetry to C_2 in the structure of gypsum and to C_s in the case of barite. As a consequence, the symmetric SO_4^{2-} stretch (ν_1) and the in-plane bending mode ν_2 (which under T_d symmetry should be infrared inactive) could become IR active although, probably, appreciably weaker than the characteristic infrared antisymmetric stretch ν_3 and the out-of-plane bending ν_4. In fact, the intensity of the band originating from the symmetric stretch could serve as a measure for the sulfate ion distortion (Petruševski, and Šoptrajanov, 1988). Clearly, in the spectrum of gypsum bands due to the modes of coordinated water* are expected to appear.

EXPERIMENTAL

The mineral samples were collected from various localities in Macedonia (gypsum: Debar, Alšar, Plešinci; barite: Zletovo). They were picked under a microscope from the ore samples. The p.a. quality synthetic analogues of gypsum and barite were used for the analysis.

The infrared spectra of the samples were recorded on a Perkin-Elmer FTIR system 2000 interferrometer using KBr pellets. Mulls in Nujol between KBr plates were also used. The Raman spectra were recorded on LABRAMINFINITY ISA Dilor.Jobin.Yvon.Spex Group HORIBA instrument using a CCD charge coupled detector – Jobin.Yvon. The GRAMS ANALYST 2000 package (GRAMS ANALYST, 1991–1993) was used in the process of recording the spectra and the necessary manipulations on the spectra were done with the aid of the GRAMS32 package (GRAMS32, 1991–1996).

MINERAL ASSOCIATIONS OF DEBAR, PLEŠINCI AND ALŠAR ORE DEPOSITES

Gypsum: Debar

Gypsum and anhydrite are situated on both sides of the Radika river near the Debar basin as well as in the region between the villages of Gorno and Dolno Kosovrasti.

Genetically, gypsum is a result of the processes of transformation of limestone influenced by thermal waters enriched by SO_3. Thereby, the anhydrite is formed by in situ substitution of $CaSO_2$, whereas the CO_2 is transported with the water solutions. Hydration is performed at lowered external pressure conditions and depth of about 100 to 150 m. The alabaster form is an intermediate product formed by hydration of the anhydrite at temperature higher than 170 °C. The process is characterized by about 30 % volume increase. Often, very nice crystal forms of gypsum are present at this deposit being formed by influence of the sulfurized thermal waters. The gypsum from this locality is very often accompanied by presence of organic matter, limestone fragments and pure sulfur.

Gypsum: Plešinci

During the final volcanic activities in the Kratovo-Zletovo region, significant quantities of pure sulfur are formed in the locality of Plešinci. From the geological point of view, this locality consists of series of volcanic and volcano-sediment rocks. Mineralization takes place along structural discontinuities in the zones of intensive hydrothermal alterations. The mineral composition of this deposit is not thoroughly studied, but the present knowledge supports the hypothesis about the low temperature mineral paragenesis with dominant role of pure sulfur. As a consequence of the great abundance of pure sulfur and carbonates along the present series of the volcano-sediment rocks, significant quantities of gypsum are formed at some parts of this locality.

Gypsum: Alšar

The Alšar mining district is located in the Kožuf Mountain in Macedonia. The district is extensively mined for its antimony, arsenic and thallium resources since 1880. The bedrock geology of the district is comprised of two distinctive chronostratigraphic sequences:

1. Mesozoic carbonate and clastic sediments.

2. Tertiary tuffaceous sediments and Pliocene felsic tuffs.

The Alšar deposit is of hydrothermal low temperature origin. The absolute age of volcanic activity is about 5 to 7 million years. Small bodies of a mineralized, porphyritic, subvolcanic intrusive

*Only one type of such molecules is present in the structure.

cross cut both Mesozoic and Tertiary rocks. Several major structural sets (northwest, northeast and northerly) dissect and juxtapose the bedrock sequence into complex contact relationships.

Two main types of mineralization occur:

1. As, Tl, Hg, Sb and SiO_2 associated with argillic clays.

2. SiO_2, Sb, Al, Tl, Hg, Au and Ba replacement silifications.

Type 1 is characterized by orpiment, realgar, lorandite, complex thallim minerals, cinabar, minor silica and stibnite.

Type 2 consists of microcrystalline quartz, stibnite, iron sulfide, falcmanite, fizelite, realgar, cinabar, Tl minerals, barite and gypsum.

Barite: Zletovo

The low temperature oxydo-carbonate paragenesis of the Zletovo locality is a final phase of the hydrothermal stadium of formation of this deposit. Low temperature minerals, mainly carbonates (siderite, calcite, oligonite, rodohrozite), sulfates (barite) and minerals of the type of quartz, opal and chalcedone are found in this deposit.

RESULTS AND DISCUSSION

Gypsum

The FTIR spectra of the gypsum mineral samples from the localities Debar (1), Alšar (2) and Plešinci (3) as well as the spectrum of its synthetic analogue (4) are shown in Fig. 1.

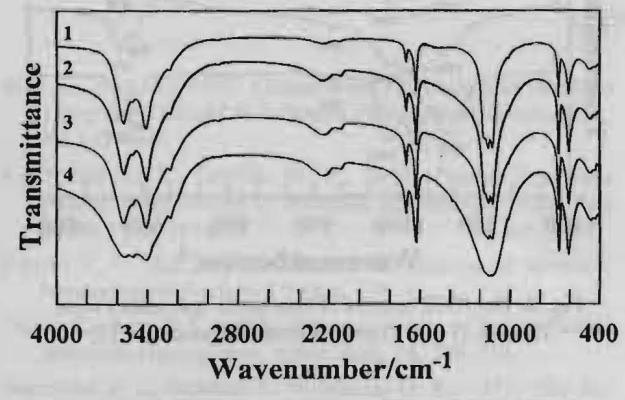

Fig. 1. The FTIR spectra of gypsum specimens from Debar (1), Alšar (2), Plešinci (3) and its synthetic analogue (4)

As can be seen, the spectra of the minerals from all three localities are practically identical indicating that the specimens belong to the same mineral species. Their comparison with published spectra of gypsum originating from localities outside Macedonia (Farmer, 1974; Takahashi *et al.* 1983; Seidl *et al.* 1969; Bensted, 1976) enabled us to characterize them as gypsum *mineral* samples. Furthermore, the spectrum of *synthetic* $CaSO_4 \cdot 2H_2O$ differs practically only in the extent of splitting of the bands originating from the water stretches and the antisymmetric SO_4^{2-} stretch ν_3, a fact which apparently stems from the more favorable conditions for crystal growth in the case of the mineral specimens.

The Raman spectra of the gypsum specimens from Alšar (1) and Debar (2), as can be seen in Fig. 2, are practically identical with the spectrum of synthetic $CaSO_4 \cdot 2H_2O$ (3). Expectedly, all four vibrational modes of the sulfate anions (ν_1, ν_2, ν_3 and ν_4) are Raman active, the symmetric stretches ν_1 giving rise to the strongest bands in the spectra. On the other hand, the ν_1 mode gives rise to a weak infrared band (at 1004 cm^{-1}).

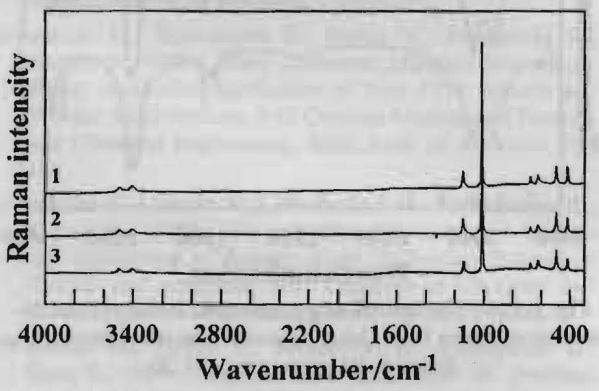

Fig. 2. The Raman spectra of gypsum from Alšar (1) and Debar (2) and its synthetic analogue (3)

In the case of gypsum spectra it is difficult to locate unequivocally the band(s) resulting from the ν_2 sulfate mode. In the region where it is to be expected (around 450 cm^{-1}) no band characteristic for this mode is observed. Actually, a broad band is found at 458 cm^{-1} in the infrared spectra of the gypsum samples (Fig. 1) but it is assigned to water librations (see below).

The bands originating from the water molecules are, of course, present in the IR spectra of both natural and synthetic $CaSO_4 \cdot 2H_2O$ (Fig. 1). Three of them (at 3552, 3492 and 3404 cm^{-1})

originate from the antisymmetric and symmetric water stretchings and, apparently, a second-order transition reinforced by Fermi resonance. The somewhat unexpected appearance of *two* bands (at 1685 and 1620 cm^{-1}) in the H–O–H bending region (unexpected because there is only one type of water molecules) is easily explained (and experimentally verified) (Seidl *et al.*, 1969) as a consequence of correlation-field effects (vibrational interaction of identical oscillators). Finally, the broad band at around 458 cm^{-1} has been attributed to water librations (Takahashi *et al.*, 1983; Petruševski, 1989; Cvetković, 1982).

As already mentioned, we have also studied a mineral specimen (from the Debar ore deposit) considered to be anhydrite ($CaSO_4$). Its FTIR (Fig. 3) and Raman spectra (Fig. 4), however, showed that it is in fact gypsum. It is interesting to mention that, compared to the other studied gypsum specimens from various localities in Macedonia, the morphological characteristics (shape, color and transparency) of our "anhydrite" are quite different. Apparently, a pseudomorphous transition from anhydrite to gypsum has taken place.

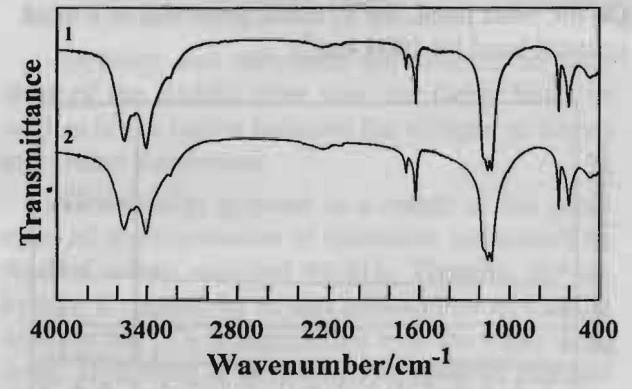

Fig. 3. The FTIR spectra of gypsum from Debar (1) and the mineral specimen from Debar believed to be anhydrite but was shown to be gypsum instead (2)

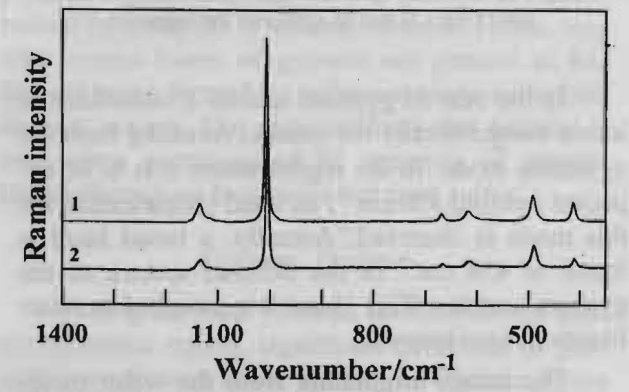

Fig. 4. The Raman spectra of gypsum from Debar (1) and the mineral specimen from Debar believed to be anhydrite but was shown to be gypsum instead (2)

Barite

The FTIR spectra of two mineral specimens collected as barite from the localitie Zletovo (1 and 2) as well as the spectrum of synthetic $BaSO_4$ (3) are shown in Fig. 5 and the Raman spectra are given in Fig. 6. The identical infrared, on one hand, and Raman spectra, on the other, of the two natural specimens Zletovo unequivocally shows that they belong to the same mineral (barite). The infrared as well as the Raman spectrum of the synthetic $BaSO_4$ is also very similar to the corresponding spectra of the natural minerals. However, the band frequencies are slightly different, the largest shift (for one of the ν_3 components) in the infrared spectra amounting to 7 cm^{-1} (Fig. 5). The frequency differences in the Raman spectra (Fig. 6) are smaller and do not exceed 3 cm^{-1}. It could be taken as an additional evidence that the studied mineral samples are $BaSO_4$.

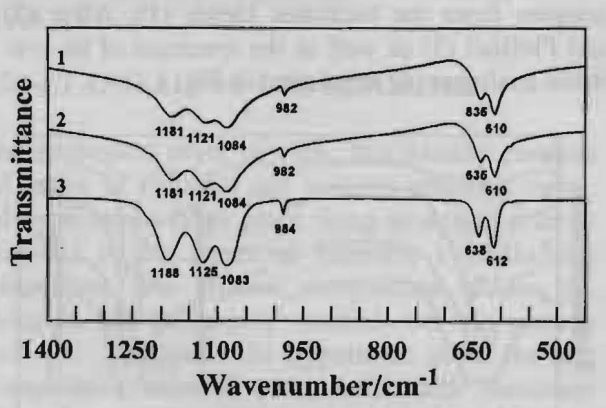

Fig. 5. The FTIR spectra of two barite specimens from Zletovo (1 and 2) and its synthetic analogue (3)

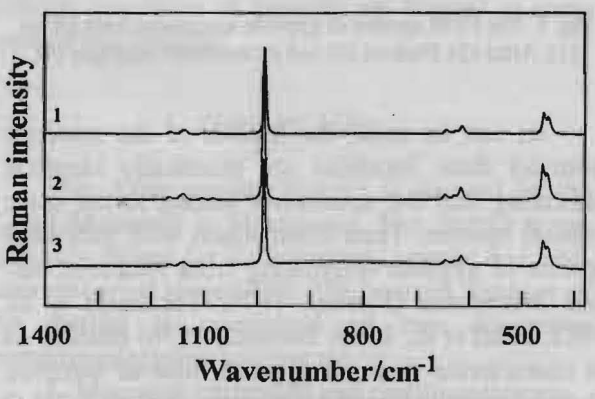

Fig. 6. The Raman spectra of two barite specimens from Zletovo (1 and 2) and its synthetic analogue (3)

As in gypsum, as a result of the lower local symmetry of the SO_4^{2-} anions in the solid state, the IR-inactive (for T_d symmetry) ν_1 and ν_2 modes should become active. In fact, a very weak infrared

band indeed appears (see Fig. 5) at 982 cm^{-1}, i.e. in the region where the ν_1 mode is expected. No band, however, can be located in the ν_2 region, irrespective of the fact that there are no water bands to obscure the region. The absence of the in-plane bending ν_2 mode in the infrared spectra of barite was interpreted as being due to the high *effective* symmetry of the force field for this mode. This explanation can be tentatively proposed in the case of gypsum as well.

CONCLUSION

It was found that the band originating from the ν_2 sulfate mode (expected at around 450 cm^{-1}) does not appear in the infrared spectra of either gypsum or barite. This was interpreted as being due to the high *effective* symmetry of the force field for this mode.

It was also shown that the IR spectra of the natural mineral gypsum and its synthetic analogue are very similar, whereas the spectrum of the synthetic barite shows some frequency differences compared to the spectrum of mineral barite (the differences being especially pronounced in the region of the ν_3 sulfate modes).

No significant differences were found between the Raman spectra of gypsum and of its synthetic analogue as well as between the Raman spectra of barite and synthetic $BaSO_4$.

The study of the IR and Raman spectra of the mineral which was previously thought to be anhydrite showed that the studied mineral is, in fact, gypsum.

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Резиме

МИНЕРАЛИ ОД МАКЕДОНИЈА
V. КАРАКТЕРИЗАЦИЈА НА ГИПС И БАРИТ И НИВНИТЕ СИНТЕТИЧКИ АНАЛОЗИ СО ПОМОШ НА FTIR-СПЕКТРОСКОПИЈА

Виктор Стефов[1], Глигор Јовановски[1*], Бојан Шоптрајанов[1], Билјана Минчева-Шукарова[1], Сандра Димитровска[1], Блажо Боев[2]

[1]Природно-математички факултет, Институт за хемија, п.фах 162, МК-1001 Скопје, Република Македонија
e-mail: gligor@pmf.ukim.edu.mk
[2]Рударско-геолошки факултет, Гоце Делчев 89, МК-2000 Штип, Република Македонија
e-mail: b.boev@rgf.ukim.edu.mk

Клучни зборови: сулфатни минерали; гипс; барит; Македонија; Фуриеова трансформна (FTIR) и раманска спектроскопија

Изучувани се Фуриеовите трансформни инфрацрвени (FTIR) и раманski спектри на гипс ($CaSO_4 \cdot 2H_2O$) и барит ($BaSO_4$) од различни локалитети во Македонија. Наспроти претскажувањата засновани на теоријата на групите, најдено е дека лентата што потекнува од ν_2 сулфатниот мод (очекувана на околу 450 cm^{-1}) не се појавува во инфрацрвените спектри на гипсот и баритот. Ова очигледно се должи на високата ефективна симетрија на силовото поле за овој мод. Инфрацрвените и раманските спектри на природниот гипс и неговиот синтетички аналог се многу слични. Од друга страна, регистрирани се мали фреквентни разлики (особено изразени во подрачјето на ν_3 сулфатните модови) помеѓу инфрацрвените, односно раманските спектри на природниот гипс и неговиот синтетички аналог, соодветно. Изучувани беа, исто така, и инфрацрвените и раманските спектри на минералот кој претходно бил карактеризиран како анхидрит. Иако неговите морфолошки карактеристики (облик, боја и прозрачност) се потполно различни од оние на природниот гипс, покажано е дека изучуваниот минерал всушност е гипс.

*Автор за кореспонденција.
Tel. +389 2 117 055; fax: +389 2 226 865
e-mail:gligor@pmf.ukim.edu.mk